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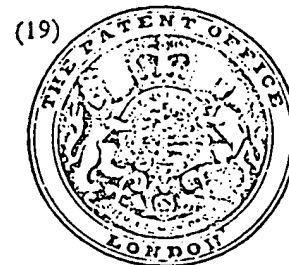
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(54) COATING OF GLASS

(71) We, BFG GLASSGROUP, a
 Groupement d'Interet Economique, estab-
 lished under the laws of France (French
 Ordinance dated 23rd September 1967), of
 Rue Caumartin 43, 75009 Paris, France, do
 hereby declare the invention, for which we
 pray that a patent may be granted to us, and
 the method by which it is to be performed,
 to be particularly described in and by the
 following statement:—

This invention relates to a process for
 forming a metal or metal compound coating
 on a face of a glass substrate by contacting
 such face while it is at elevated temperature
 with a gaseous medium consisting of or con-
 taining a substance or substances in gaseous
 phase, which substance(s) undergo(es) chemi-
 cal reaction or decomposition to form said
 metal or metal compound on said face. The
 invention also relates to apparatus for use
 in carrying out such a process.

Processes of the above kind are employed
 for forming coatings which modify the
 apparent colour of the glass and/or which
 have some other required properties in re-
 spect of incident radiation, e.g. an infra-
 red-reflecting property.

The known processes do not always enable
 coatings with satisfactory properties to be
 achieved. Difficulties are encountered in
 forming coatings sufficiently quickly to keep
 pace with industrial production programmes
 and/or in forming coatings which are of satis-
 factory quality e.g. in respect of their uni-
 formity of thickness and their optical prop-
 erties.

The subject of the patent application is a
 coating process which affords important
 advantages in respect of the reliability with
 which good quality coatings can be formed
 and/or of the high coating rates which are
 attainable.

The process according to the invention,
 which is of the kind above referred to, is
 characterised in that the gaseous medium is
 caused to flow along the substrate face to
 be coated as a substantially turbulence-free
 layer along a flow passage which is defined in
 part by the face of the glass and which leads

to an exhaust ducting via which residual
 medium is drawn away from said face.

One factor contributing to the good results
 realisable by this process is the establishment
 of a substantially turbulence-free flowing layer
 of the gaseous medium in contact with the
 face to be coated. The flow of gaseous medium
 along the flow passage is considered sub-
 stantially turbulence-free if it is substantially
 free of local circulating currents or vortices
 giving rise to a substantial increase in the
 flow resistance. In other words, the flow is
 preferably laminar but undulation of the fluid
 or minor eddy currents can be tolerated pro-
 vided that the required coating metal or metal
 compound is formed substantially only at the
 boundary layer in contact with the hot sub-
 strate surface and is not to any significant
 extent formed as a precipitate within the fluid
 stream.

Experiments indicate that as compared
 with hitherto known processes, the process
 according to the invention makes it easier to
 form a coating, e.g. a metal oxide coating,
 providing a uniform coverage of the substrate
 surface. The superiority of the new process
 appears to be particularly evident when
 attempting to build up coatings rapidly e.g. at
 a rate of at least 700 Å of coating thickness
 per second. The invention therefore promises
 to be of special importance when coating glass
 ribbons, in course of continuous production
 at high speeds, e.g. speeds in excess of 2
 metres per minute and even in excess of 10
 metres per minute such as are often attained
 by the float process.

The avoidance of spurious deposits on the
 substrate surface are more easily avoided if
 the flow passage within which the coating is
 formed is shallow. Preferably the height of
 the flow passage measured normally to the
 substrate face is at no point in excess of
 40 mm.

The flow passage may be of uniform height
 or the passage may increase or decrease in
 height along its length in the direction in
 which the gas flow takes place.

It is advantageous for the height of the
 flow passage to decrease in the direction of
 gas flow therethrough, at least over an end

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portion of its length leading up to the exhaust ducting. By using a flow passage which tapers in that manner it is easier to avoid objectionable turbulence within the flowing layer of gas. Preferably the flow passage tapers over at least the greater part of its length. An angle of taper of 10° or less is usually satisfactory.

For achieving the best results it is always desirable for the coating to be formed progressively, on successive incremental portions of the substrate face. The invention can be applied for continuously coating a face of a continuous ribbon of glass and in that case it is of course inevitable that the flow passage will occupy only a portion of the length of the said face and the flow passage and substrate must be relatively displaced as the process proceeds. However even when coating a sheet, it is preferable for the flow passage to occupy only an incremental portion of at least one dimension of the face area to be coated and to bring about relative displacement of the flow passage and substrate so as to form the coating progressively on successive portions of the face.

Preferably the aforesaid relative displacement occurs in a direction parallel with the direction in which gas flows along the flow passage. In this case all of the successively coated portions of the face are exposed to the same coating conditions integrated over the length of the flow passage. However in some cases good results can be obtained by bringing about such relative displacement in a direction normal to the said gas flow direction along the substrate. For example for coating a sheet the flow passage may extend along one dimension of the sheet and extend across only a portion of the other dimension of the sheet and the latter can be displaced parallel with that other dimension.

The advantages of this process according to the invention are particularly notable when the process is employed for coating the top face of a ribbon of glass which is in continuous movement at a speed of at least 2 metres per minute, parallel with its longitudinal axis and in the direction of the gas flow through the aforesaid gas flow passage. The flow passage can be quite short, which is an important consideration in view of the limited space which is available in many plants for the production and treatment of continuous glass ribbons. Generally it is preferable for the length of the flow passage (i.e. its dimension measured in the direction of gas flow therethrough) to be not more than 2.0 metres. The length of the flow passage is however preferably in all cases not less than 10 cm.

The invention has been made primarily with a view to the formation of good quality metal oxide coatings on glass substrates. However the invention can be applied for forming coatings of other metal compounds e.g. for

forming a coating of a metallic boride, sulphide, nitride, carbide or arsenide by reacting a corresponding metallic or organometallic compound with a halogenated boron compound, H_2S , NH_3 , CH_4 , or an arsenic containing compound, in the absence of oxygen. The invention can also be applied for forming a metal coating. For example a coating of nickel can be formed by decomposing nickel carbonyl under the action of heat provided by the heated substrate, in a reducing atmosphere or at least in the absence of oxygen.

For forming a metal oxide coating, the invention includes processes wherein a stream of oxygen or oxygen-containing gas and a separate stream of a vaporised metal compound with which oxygen reacts to form a metal oxide coating on the substrate face are caused to flow continuously into said flow passage. A particular and important embodiment of the invention performed in that way employs a stream of a vapourised tin compound and a stream or streams of oxygen-containing gas for forming a tin oxide coating.

However various other metal oxide coatings can be formed in that manner, e.g. a coating of titanium dioxide by reacting titanium tetrachloride with oxygen. The vapourised metal compound will usually be diluted with an inert gas, e.g. nitrogen and the vapour stream may contain additional ingredients for modifying the properties of the coating. For example the vapour stream may contain antimony pentachloride for forming antimony dioxide together with the principal oxide ingredient of the coating.

In certain processes as above referred to for forming a metal oxide coating, a gas stream consisting of or containing a said vapourised metal compound is continuously discharged into the aforesaid flow passage and induces a flow of air into and along such passage.

In some cases the gaseous medium entering the flow passage comprises a layer of vapourised metal compound and a layer of oxidising gas which flows between said layer of vapourised metal compound and the substrate face being coated. When proceeding in that way, the flow of oxidising gas, e.g. air, beneath the layer of vapourised metal compound, promotes rapid formation of the coating so that it commences to form on the substrate at or near the entry end of the flow passage.

In an alternative procedure, the gaseous medium entering the flow passage comprises an upper layer of oxidising gas and a layer of vapourised metal compound which flows beneath such upper layer. The vapourised metal compound may enter the passage in contact with the face of the substrate in which case the upper layer of oxidising gas

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tends to prevent the stream of vapourised metal compound from flowing upwardly away from the face of the substrate. A particularly advantageous feed system is one wherein a stream of vapourised metal compound enters the flow passage between overlying and underlying streams of oxidising gas. The result is that the stream of vapourised metal compound is depressed away from the top surface of the flow passage, so avoiding or reducing tendency for oxide deposition to occur on such surface, while at the same time a rapid formation of the metal oxide coating on the glass substrate is promoted by the lower stream of oxidising gas.

As has already been indicated, it is an advantage of the invention that good quality coatings can be formed very rapidly. This potential advantage is realised in embodiments of the process wherein the composition of the gaseous medium flowing through the flow passage and the temperature conditions to which such medium is exposed are such that the coating forms on the substrate face at a rate of at least 700 Å per second. The process as thus performed can be applied for forming optical coatings on a fast moving glass ribbon, e.g. a ribbon advancing through the coating zone, at a speed of 2 metres per minute or more e.g. greater than 10 metres per minute such as is often attained in the float process.

The invention includes a process for coating a continuous ribbon of glass which is in movement parallel with its longitudinal axis and in the same direction as the direction of gas flow along said flow passage, characterised in that the gaseous medium flowing along said flow passage derives at least in part from a gas stream which enters said passage from a path which is at an angle of 45° or less to said face. Such a process can be performed quite conveniently in many existing flat glass production plants because a conduit or conduits for delivering the gas can be installed with little or no modification of the plant lay-out. The delivery of the or a gas stream at an angle of 45° or less to the face to be coated is moreover conducive to the formation of a coating of relatively homogeneous or uniform structure, e.g. a structure featuring a regular arrangement of crystals.

The discharge of gases into the flow passage at an acute angle to the ribbon is favourable also for promoting the required non-turbulent flow of gaseous medium along the flow passage. If a process according to the invention is carried out so that the gaseous medium flowing along such passage derives from two or more gas feed streams separately discharged into said passage one above another, a nicely controlled flow of the medium along the passage can be achieved even if one or more but not all of such feed streams discharge(s) at an angle of less than 45° to

the ribbon but for the best results it is preferable for the mean angle of such discharging streams with respect to the ribbon to be less than 45°. In certain embodiments of the invention, the gaseous medium flowing along the flow passage derives from gas feed streams of different compositions which enter the passage from paths which are at an angle of 20—35° to each other.

The discharge of gas streams into the flow passage at an inclination to the substrate as above described is a feature which can be adopted with advantage when coating an individual glass sheet or a part thereof. However, depending on circumstances in a given industrial plant, there will usually not be such a restricted choice of positions for the gas feed conduits as there is in a flat glass forming apparatus. When coating an individual sheet, one or more gas streams can be discharged into the flow passage parallel with the sheet if so required.

Preferably the exhaust ducting is in the form of a chimney extending upwardly away from the substrate face being coated. The manner in which the flow takes place along the flow passage is influenced by the suction forces which exist at the exit of such flow passage. The use of a chimney extending upwardly away from the face has been found to be very beneficial for the quality of the coating. Other arrangements of the exhaust ducting are however possible. For example the ducting may be arranged so that gases reaching the exit end of the flow passage are drawn off laterally through one or more transverse ducts. This is feasible particularly if the entry end portion of the ducting is subdivided into a series of side by side passageways as hereafter referred to.

Advantageously, an exhaust ducting is used comprising a plurality of separate passageways distributed in side by side relationship across substantially the whole width of the gas flow path through the flow passage. The exhaust of gas via different exhaust ducting passageways or through different groups of passageways may be independently controlled e.g. by means of independently controllable extractors, for achieving a required volume flow rate profile across the width of the flow passage.

Particular importance is attached to the performance of a process according to the invention for coating a ribbon of glass progressing from a float tank and in that field of application preference is given to processes in which the flow passage is located downstream of the exit end of the float tank and at a zone where the glass has a temperature in the range 100° to 650°C.

The invention includes apparatus suitable for use in carrying out a coating process according to the invention as hereinbefore defined. Apparatus according to the invention

by partitions such as 18 into a plurality of exhaust passageways distributed in side by side relationship across substantially the whole width of the gas exhaust path.

A vapour mixture containing SnCl_4 and SbCl_3 was generated from a liquid phase containing such ingredients in a volume ratio of 100:1 and this vapour mixture, entrained in a stream of nitrogen, was delivered from vessel 11 through the feed channel 12.

The temperature of the glass ribbon at the region beneath the entry end of the flow passage 13 was about 585°C .

The rate of delivery of the vapour mixture into the flow passage 13 and the draught forces through the chimney 15 were regulated so as to establish along said passage a substantially turbulence-free flow of vapour mixed with air induced into the passage by the discharge of the vapour stream, as suggested by the arrows beneath the feed channel 12. Such regulation was moreover such that a coating composed essentially of SnO_2 together with a small quantity of Sb_2O_3 , serving as doping agent, and having a thickness of $2,500 \text{ \AA}$, was formed on the travelling glass ribbon. Regulation of the draught forces can be achieved e.g. by using a regulatable fan in the chimney 15.

The coating on the glass had a green tint viewed by reflected light. The coated glass had a very high visible light transparency but reflected a significant proportion of incident radiation in the far infrared spectral region.

The emissivity of the coating was 0.4; its diffuse luminous transmission was practically nil.

Examination of the coating showed that it had an homogeneous structure and had uniform thickness and optical properties.

A coating method as above described can be performed in the same way for coating a continuous ribbon of sheet glass travelling from the drawing chamber of a Libbey-Owens type drawing machine. For example the compartment 4 can equally well be regarded as located within the annealing gallery adjoining such drawing machine.

Example 2

A coating process was performed in the same way as Example 1 but the vapour mixture forming the coating composition derived from a solution of stannous acetate and a small proportion of SbCl_3 in glacial acetic acid, the SbCl_3 being added as doping agent.

The vapour mixture from this solution was entrained into contact with the glass ribbon in a stream of nitrogen from which all traces of oxygen had been removed. The glass ribbon had a temperature of about 585°C at the place of initial contact by the vapour mixture. The glass ribbon speed was 6 metres per minute.

A coating of SnO_2 together with a small quantity of antimony oxide and having a thickness of 4000 \AA , was formed on the glass ribbon. The delivery rate of the vapours along feed channel 12 and the draught forces through the chimney 15 were regulated so that the vapours were maintained in substantially turbulence-free flow along flow passage 13 and the coating oxides were formed substantially only at the boundary layer of vapour in contact with the hot glass ribbon.

The coating had a greenish tint, viewed by reflected light. The coating had a high transparency to light in the long wavelength region of the visible spectrum and reflected a significant proportion of incident radiation in the far infrared wavelength band.

The emissivity of the layer was 0.3. The diffuse luminous transmission of the coating was practically nil.

The thickness of the layer and its optical properties appeared to be truly uniform and its structure was homogeneous over the whole area of the coating.

In another process according to the invention, coatings of good quality were formed by following a procedure as just described but using as the feed stock vapours of ZrCl_4 entrained in a stream of dry air. A layer of ZrO_2 was formed having a grey tint viewed by reflected and by transmitted light.

Example 3

Using a coating apparatus as represented in Figs. 1 and 2 and described in Example 1, vapours of titanium isopropylate



entrained in a current of nitrogen were delivered through the feed channel 12, to contact a glass ribbon where its temperature was about 605°C . The ribbon speed was 7 metres per minute.

The rate of delivery of the vapour mixture and the aspiration of gases from the flow passage 13 into the chimney 8 were regulated so as to establish a substantially non-turbulent vapour flow along passage 13 and so that a coating layer of TiO_2 having a thickness of 550 \AA was formed on the glass ribbon.

The coating appeared white by reflected light. The refractive index of the coating was 2.49. The diffuse luminous transmission of the coated glass was practically nil.

Examination of the coating showed that its thickness, structure and optical properties were substantially uniform.

Example 4

Coating apparatus as represented in Fig. 3 was used for coating a glass ribbon 19 during its conveyance on rollers 20 through a compartment 21 of a gallery having refractory

roof and sole walls 22, 23. The compartment 21 has end walls formed by displaceable refractory screens 24, 25. The coating apparatus comprises a shroud 26 defining with the top face of the longitudinally moving glass ribbon 19 a shallow gas flow passage having a length of 40 cm and a uniform height of 15 mm extending over substantially the full width of the glass ribbon. Twin feed channels 27 and 28 lead from gas reservoirs 29 and 30 respectively into the entry end of the horizontal flow passage beneath the shroud 26. The feed channel 27 is inclined at an angle of 30° to the glass ribbon whereas the angle of inclination of the feed channel 28 is 50° . At its exit end the horizontal flow passage is subdivided by vanes such as 31 into a plurality of side by side exit portions which lead into exhaust ducting 32. This ducting comprises two horizontal exhaust tubes disposed at right angles to the longitudinal axis of the shroud 26 and leading in opposite directions therefrom. Each of such tubes was provided with an extractor fan (not shown).

A ribbon of glass was conveyed through the coating station at a speed of 17 metres per minute. The temperature of the glass at the coating station was 580°C . Vapours of iron acetylacetonate entrained in a current of dry nitrogen were fed along feed channel 27. A current of oxygen was delivered along feed channel 28. The rate of feed of the gases through the feed channels 27 and 28 and the aspirating forces acting via the exhaust ducting were regulated in such manner that the mixture of gases deriving from feed channels 27 and 28 was maintained in substantially turbulence free flow along the flow passage beneath shroud 26 and a coating of Fe_2O_3 having a thickness of about 500 Å was formed on the glass ribbon. The coating appeared yellow-amber by transmitted light. Examination of the coating showed that its

structure was homogeneous and that it had uniform thickness and optical properties.

By appropriate choice of the starting materials a coating of cobalt oxide can be formed in a similar manner. By employing a suitable mixture of vapours, coatings having different colourations and comprising a mixture of oxides, e.g., a mixture of oxides in the group Fe_2O_3 , Co_2O_3 , and Cr_2O_3 can be formed.

In the above coating method the gallery in which the compartment 21 is located is an annealing gallery connected to a float tank. This coating method could also be performed for coating a ribbon of float glass before admission in the annealing gallery. It could as well be performed for coating a glass ribbon of some other origin, e.g. a ribbon formed in a Libby Owens drawing machine.

Coating apparatus as described with reference to Fig. 3 could be employed in a similar manner for coating individual sheets of glass during their transportation through a coating station.

Example 5

By means of apparatus as used as shown in Fig. 3 coatings of various compositions, of uniform thickness and optical properties, and having an homogeneous structure were formed on ribbons of glass in course of their manufacture.

The Table below gives the reactants employed for forming such coatings, also the temperature of the glass on contact thereof by the reactants the composition of the formed coating and certain properties thereof.

In each case dry nitrogen was employed as inert carrier for the reactants, and the coating was effected in an environment free from oxygen. The coated glass was kept out of contact with air until the temperature of the glass was sufficiently low to avoid risk of chemical modification of the coating.

TABLE

	1st Reactant, fed through passage 27	2nd Reactant, fed through passage 28	Glass Temp. $^\circ\text{C}$.	Composition of formed coating	Properties of coating
90	$\text{Pb}(\text{C}_2\text{H}_3)_2$	H_2S	200	PbS	Grey in reflection, yellow-brown in transmission, for thickness of 500 Å
95	SiH_4	NH_3	600	Si_3N_4	Very chemically stable; refractive index near that of glass; thus nearly invisible
	$\text{Cr}(\text{CO})_3$	CH_4	150	Cr_2C_3	Hard; acid resistant; light-reflecting grey-neutral in transmission
100	$\text{Ga}(\text{CH}_3)_3$	$(\text{CH}_3)_3\text{AsCN}$	250	GaAs	Semi-conductive

Sheets of glass can be coated under the same conditions.

Example 6

A ribbon of glass was coated using apparatus as represented in Fig. 3. On reaching the

coating station the glass ribbon had a temperature of 600°C . The ribbon was exposed at the coating station to an atmosphere free from oxygen and enriched in hydrogen.

Vapours of vanadium chloride (VCl_3) entrained in a stream of hydrogen were fed to

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the glass along feed channel 27. Boron bromide vapours (BBr_3) entrained in a stream of hydrogen were fed through feed channel 28.

5 At a coating zone within the shroud 26 a coating of vanadium boride (VB_2) formed on the glass ribbon. The coating appeared grey. The successively coated portions of the ribbon were not brought into contact with air until their temperature had fallen sufficiently to avoid risk of chemical modification of the coating.

10 Coatings of metallic silicon can be formed in similar manner by exposing the glass while at a temperature of 500°C to vapours of silicon hydride (SiH_4). In such a process it is essential to protect the coating from oxidation.

15 Individual sheets of glass can be coated under the same conditions.

Example 7

20 Sheets of glass were coated in an apparatus as shown in Fig. 4. The glass sheets, one of which is shown and is designated 33, were placed on a conveyor 34 and transported thereby through a coating station. The glass sheets on reaching such station had a temperature of approximately 200°C .

25 At this coating station there is an enclosure (not shown) through which the conveyor 34 passes and within this enclosure there is a gas flow passage 35 through which a gas stream containing the precursor of the coating material is caused to flow in contact with the glass, in a direction transverse to the direction of movement of the glass sheets. A feed channel 36 leads horizontally to such flow passage from an entrance shaft 37. Surplus gases leaving passage 35 escape through exhaust ducting 38 the entry end of which is internally subdivided by partitions 39 into a plurality of side by side flow paths.

30 The length of the flow passage 35 (i.e. its dimension normal to the direction of movement of the glass sheets) is 1 m and its height is 20 mm.

35 The aforesaid enclosure at the coating station was kept filled with nitrogen, to the exclusion of oxygen, at slightly above atmospheric pressure in order to avoid inducement of air into the coating zone. Nickel carbonyl vapours, entrained in a stream of nitrogen were delivered through feed channel 36. The rate of delivery of this feed stock and the rate of extraction of surplus gases through the exhaust ducting 38 were such as to establish a substantially turbulence-free flow along the passage 35 and ensure that a coating was formed on the surface of the glass sheets, which coating was formed substantially exclusively by the decomposition of the organic substance at the boundary layer of vapour in contact with the hot glass sheets. The result was that a coating of nickel 100 Å in thick-

ness, was formed on each glass sheet. The coatings appeared grey by transmitted and by reflected light. Each coating was of uniform thickness and had uniform structure and optical properties. The coatings uniformly transmitted light over a broad visible wavelength band. The coatings showed minimal diffuse luminous transmission.

By the control of the atmosphere to which the coatings formed on the sheets were exposed at the coating station and by keeping the temperature of the glass sheets on leaving the coating station sufficiently low, modification of the coatings on contact with air was avoided.

WHAT WE CLAIM IS:—

1. A process of forming a metal or metal compound coating on a face of a glass substrate by contacting such face while it is at elevated temperature with a gaseous medium consisting of or containing a substance or substances in gaseous phase, which substance(s) undergo(es) chemical reaction or decomposition to form said metal or metal compound on said face, characterised in that said gaseous medium is caused to flow along said face as a substantially turbulence-free layer along a flow passage which is defined in part by the face of the glass and which leads to an exhaust ducting via which residual medium is drawn away from said face.

2. A process according to claim 1, characterised in that the height of said flow passage, measured normally to said face, is at no point in excess of 40 mm.

3. A process according to claim 1 or 2, characterised in that said flow passage tapers in the direction of gas flow therethrough, at least over an end portion of its length leading up to said exhaust ducting.

4. A process according to any preceding claim, characterised in that said flow passage occupies only an incremental portion of at least one dimension of the area to be coated and said flow passage and said substrate are relatively displaced so that the coating is formed progressively, on successive portions along said face.

5. A process according to claim 4, characterised in that said relative displacement occurs in a direction parallel with the direction in which the gas flows along said flow passage.

6. A process according to claim 5, characterised in that said face is the top face of a ribbon of glass which is in continuous movement at a speed of at least 2 metres per minute, parallel with its longitudinal axis and in the direction of said gas flow.

7. A process according to claim 6, characterised in that the length of said flow passage (i.e. its dimension measured in the direction of gas flow therethrough) is not more than 2.0 metres.

8. A process according to claim 7, characterised in that the length of said flow passage (i.e. its dimension measured in the direction of gas flow therethrough) is not less than 10 cm.

9. A process according to any preceding claim, characterised in that a stream of oxygen or oxygen-containing gas and a separate stream of a vapourised metal compound with which oxygen reacts to form a metal oxide coating on said face feed continuously into said flow passage.

10. A process according to claim 9, characterised in that said gaseous medium contains a vapourised tin compound and a tin oxide coating is formed on said face.

11. A process according to claim 9 or 10, characterised in that a gaseous medium consisting of or containing a said vapourised metal compound is continuously discharged into said flow passage and induces a flow of air into and along such passage.

12. A process according to any of claims 9 to 11, wherein the gaseous medium entering said flow passage comprises a layer of vapourised metal compound and a layer of oxygen-containing gas which is introduced between said layer of vapourised metal compound and said face.

13. A process according to any of claims 9 to 12, wherein the gaseous medium entering said flow passage comprises an upper layer of oxygen-containing gas and a layer of vapourised metal compound which flows beneath such upper layer.

14. A process according to any preceding claim, characterised in that the composition of said medium and the temperature conditions to which it is exposed are such that said coating forms on said face at a rate of at least 700 Å per second.

15. A process according to any preceding claim, applied for coating a continuous ribbon of glass which is in movement parallel with its longitudinal axis and in the same direction as the direction of gas flow along said flow passage, characterised in that the gaseous medium flowing along said flow passage derives at least in part from a gas stream which enters said passage from a path which is at 45° or less to said face.

16. A process according to claim 15, characterised in that the gaseous medium flowing along said flow passage derives from two or more gas feed streams which enter said passage from paths whose average angle to said face is 45° or less.

17. A process according to claim 15 or 16, characterised in that the gaseous medium flowing along said flow passage derives from gas feed streams of different compositions which enter said passage from paths which are at an angle of 20—35° to each other.

18. A process according to any preceding claim, characterised in that said exhaust duct-

ing is in the form of a chimney extending upwardly away from said face.

19. A process according to any preceding claim, characterised in that said exhaust ducting comprises a plurality of separate passageways distributed in side by side relationship across substantially the whole width of the gas flow path through said flow passage.

20. A process according to claim 19, characterised in that the exhaust of gas via different exhaust ducting passageways is separately controlled.

21. A process according to any preceding claim, characterised in that said substrate is a ribbon of glass formed by the float process and said flow passage is located downstream of the exit end of said tank and at a zone where the glass has a temperature in the range 100° to 650°C.

22. Apparatus suitable for use in forming a metal or metal compound coating on a face of a glass substrate by contacting such face while it is at elevated temperature with a gaseous medium consisting of or containing a substance or substances in gaseous phase, which substance(s) undergo(es) chemical reaction or decomposition to form said metal or metal compound on said face, said apparatus comprising means for supporting said substrate, means for heating such substrate, means for feeding gaseous medium into a space to which such face is exposed, and means for exhausting unused medium from such space, characterised in that the apparatus includes a shroud which is mounted in a position such that it defines with the substrate face to be coated a shallow flow passage, in that said feeding means is arranged for discharging gaseous medium into such flow passage at one end thereof, and in that the opposite end of said shallow flow passage leads into exhaust ducting via which residual medium can be drawn away from such passage.

23. Apparatus according to claim 22, characterised in that the spacing of said shroud from said substrate supporting means is such that when a substrate is in position for coating, the height of the shallow flow passage, measured normally to said face, is at no point in excess of 40 mm.

24. Apparatus according to claim 22 or 23, characterised in that said flow passage tapers towards said opposite end thereof.

25. Apparatus according to any of claims 22 to 24, characterised in that means is provided for displacing a substrate, while supported by said substrate supporting means, relative to said shroud and in the same direction as that in which gas flows along said shallow flow passage.

26. Apparatus according to claim 25, characterised in that the length of said shallow flow passage (i.e. its dimension measured in the direction in which gas flows therethrough)

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ding		is not more than 2.0 metres and not less than 10 cm.		34. Apparatus according to claim 33, characterised in that the exhaust ducting comprises a plurality of separate exhaust passageways distributed in side by side relationship across substantially the whole width of the gas flow path through said shallow flow passage.	45
Jing		27. Apparatus according to any of claims 22 to 26, characterised in that said gas feeding means comprise at least one conduit disposed for discharging gaseous medium into said shallow flow passage and consequently inducing a flow of ambient air into said passage.	5	35. Apparatus according to claim 34, characterised in that means is provided for independently controlling the exhaust of gases through said separate exhaust passageways.	50
uct-	70	28. Apparatus according to any of claims 22 to 27, characterised in that said gas feeding means comprises at least two conduits disposed for discharging streams of gases into said shallow flow passage as flow layers disposed one above the other.	10	36. Apparatus according to any of claims 22 to 35, characterised in that said substrate supporting means is adapted to support a ribbon of glass having a width of at least 2 metres and moving parallel with its longitudinal axis, and in that the corresponding dimension i.e. the widthwise dimension of said shallow flow passage is at least 1.8 metres.	55
age-		29. Apparatus according to any of claims 22 to 28, characterised in that said gas feeding means comprises at least one conduit disposed for discharging a stream of gas into said shallow flow passage at an inclination of less than 45° to the substrate face to be coated.	15	37. Apparatus according to any of claims 22 to 36, characterised in that it is disposed downstream of a float tank for use in the manufacture of a ribbon of glass by the float process, for coating the upper face of a said ribbon where the glass has a temperature in the range 100° to 650°C.	60
ship		30. Apparatus according to claim 29, characterised in that said gas feeding means comprises two or more conduits disposed for discharging streams of gas into said shallow flow passage along paths whose average angle to the substrate face to be coated is 45° or less.	20	38. A process of forming a metal or metal compound coating on a face of a glass substrate, as claimed in claim 1 and substantially according to any of the Examples herein.	65
the		31. Apparatus according to claim 29 or 30, characterised in that the gas feeding means comprises conduits disposed for discharging streams of gas into said shallow flow passage along paths which are at an angle of 20—35° to each other.	25	39. Apparatus suitable for use in forming a metal or metal compound coating on a face of a glass substrate, as claimed in claim 22 and substantially as herein described with reference to the accompanying drawings.	70
rac-	75	32. Apparatus according to any of claims 22 to 31, characterised in that said exhaust ducting is in the form of a chimney extending upwardly away from said face.	30		75
rent		33. Apparatus according to claim 32, characterised in that the rear of said chimney slopes upwardly and rearwardly from the bottom thereof relative to the chimney front.	35		80
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